OXYGEN ISOTOPES IN THE SOLAR SYSTEM: WHITHER SELF-SHIELDING. A. M. Davis. Department of the Geophysical Sciences, Enrico Fermi Institute and the Chicago Center for Cosmochemistry, University of Chicago, Chicago, IL 60637 (a-davis@uchicago.edu).

Introduction: Until a few years ago, it was widely believed that non-mass-dependent variations of oxygen isotopes within the solar system were due to variations in the isotopic composition of the gas and dust of the solar nebula that arose from nucleosynthesis in different kinds of stars [1]. There has long been a minority view that these variations were caused by symmetry-related photochemical reactions occurring in the solar nebula [2], but another photochemical effect, self-shielding of CO has gained currency. There are now three models that make use of self-shielding of UV photons by CO to produce isotopic anomalies in oxygen isotopes. Clayton [3] proposed that it occurs close to the Sun, at the X-point in the X-wind model of the solar nebula [4], where typical temperatures are 1500K. Lyons and Young [5] propose that self-shielding occurred at the surface of the solar nebula a few tens of AU from the Sun, where typical temperatures are 50–100K. Yurimoto and Kuramoto [6] propose that the isotopic variations are inherited from molecular clouds, where self-shielding of CO is known to occur, and the temperature is ~10K.

Most recent work on self-shielding of CO has concentrated on the band at ~105 nm, because this was identified as the most important band for self-shielding in molecular clouds [7]. Line-broadening effects are explored for this band: preliminary work indicates that such effects place limits on the temperature at which CO self-shielding can be effective at producing non-mass-dependent fractionation effects in oxygen.

Line Broadening: Self-shielding depends on shifts in the absorption wavelength of the different isotopomers of CO. There are several effects that control the peak shape of the UV lines that are effective at dissociating CO. It is important to consider the shape of the tails of the lines of abundant $^{12}C^{16}O$ and their effects on self-shielding of the less abundant other isotopomers.

Doppler broadening. The motions of molecules in a gas along the line of sight can cause shifting of the wavelength of absorption by the Doppler effect. The degree of Doppler broadening increases with temperature. The shape of a single line is described by

$$f_G(x) = \sqrt{\frac{2}{\pi}} \frac{1}{\Gamma_G} \exp\left[-2\frac{(x-x_0)^2}{\Gamma_G}\right],$$

where x is the wavelength in nm, x_0 is the wavelength of the line and Γ_G is the half-width at half maximum of this Guassian curve, given by

$$\Gamma_G = x_0\sqrt{2\ln 2}\sqrt{\frac{kT}{mc^2}},$$

where k is the Boltzmann constant, T is temperature, m is the mass of CO and c is the speed of light. Although the linewidth due to Doppler broadening increases with temperature, the tails drop off steeply (Fig. 1).

Natural linewidth. The Heisenberg uncertainty principle states that for states with extremely short lifetimes, there is an uncertainty in the energy (wavelength). The half-width at half maximum is given by

$$\Gamma_L = \frac{h}{2\pi\tau},$$

where h is the Planck constant and τ is the lifetime in seconds. The peak shape is described by a Lorentzian:

$$f_L(x) = \frac{2}{\pi\sqrt{3}}\frac{1}{\Gamma_L}\left/1+\frac{(x-x_0)^2}{\Gamma_L}\right..$$

The half-width at half-maximum is typically only a tenth of the Doppler broadening half-width at high temperature, but the tails fall off much more gradually (Fig. 1).
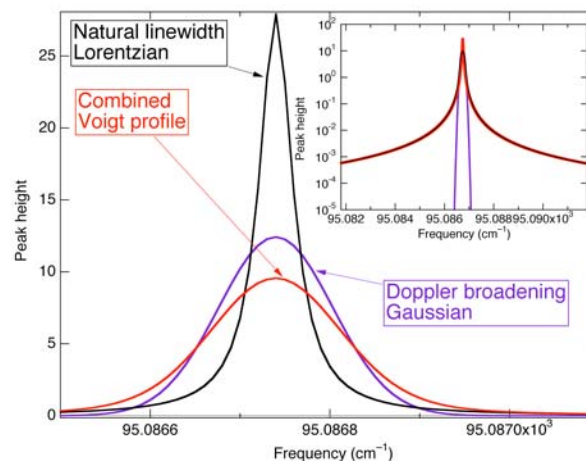

Fig. 1. Line shapes assuming constant area.

Pressure broadening. This is also described by a Lorentzian, but the effect is neglible compared to the natural linewidth for plausible conditions (P<0.01 atm).

Synthetic CO Spectra: The Gaussian and Lorentzian line profiles can be combined in the Voigt profile (Fig. 1). Synthetic spectra as a function of temperature were calculated for all six CO isotopomers for the band at 95000 cm^{-1}, labeled band 37 [8]. In molecular clouds, this band is responsible for 60% of the self-shielding effect in CO [7]. Molecular constants were taken from [9]. Terrestrial abundances were assumed for C and O isotopes. In order for self-shielding to occur, light at a particular wavelength cannot be obscured by another isotopomers. When this occurs, a condition known as mutual shielding prevails, which is much less effective at non-mass-dependent isotopic fractionation.
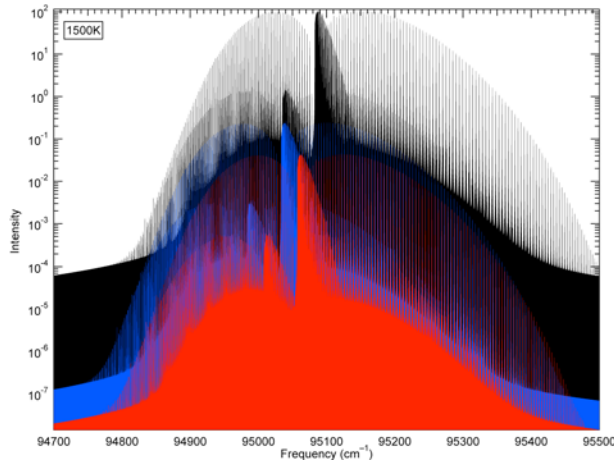
Fig. 2. Synthetic absorption spectrum for CO band 37 at 1500K. $^{12}C^{16}O$ and $^{13}C^{16}O$, or $C^{16}O$ is in black, $C^{17}O$ in red and $C^{18}O$ in blue.

1500K. The first example is at 1500K, a temperature typical of the X-point [3] (Fig. 2). The high temperature leads to many states being populated and many lines. None of the peaks for $C^{17}O$ is higher than the valleys for $C^{16}O$. The fraction of each isotopomer that is not mutually shielded by another isotopomer is: $C^{16}O$–99.8%; $C^{17}O$–0.0% and $C^{18}O$–6.2%. It seems unlikely that self-shielding of CO at 1500K will lead to $^{17}O/^{16}O$ fractionation, although some $^{18}O/^{16}O$ fractionation is possible.
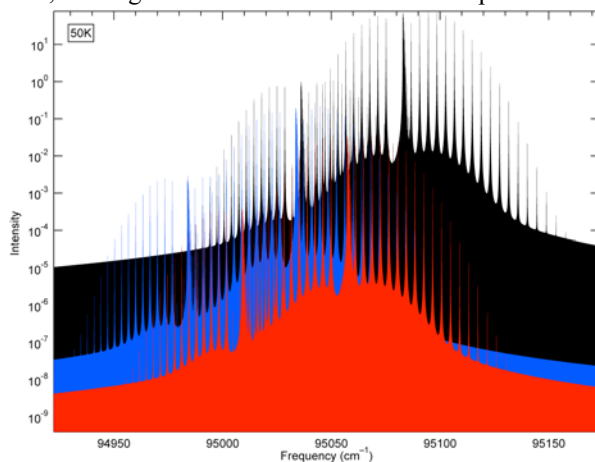

Fig. 3. Synthetic absorption spectrum for CO band 37 at 50K. Colors are the same as in Fig. 2. Note the change in scale on the horizontal axis compared to Fig. 2.

50K. The temperature at the surface of the solar nebula at distances of a few tens of AU, where Lyons and Young [5] propose self-shielding occurs, is estimated to be 50–100K. A synthetic spectrum for 50K is shown in Fig. 3. There are not nearly as many lines as at 1500K, and some $C^{17}O$ is not mutually shielded. The fraction of each isotopomer that is not mutually shielded by another isotopomer is: $C^{16}O$–99.9%; $C^{17}O$–13.1% and $C^{18}O$–86.3%. Here, self-shielding can occur, but perhaps not along a slope ~1 line on a three-isotope plot. Higher

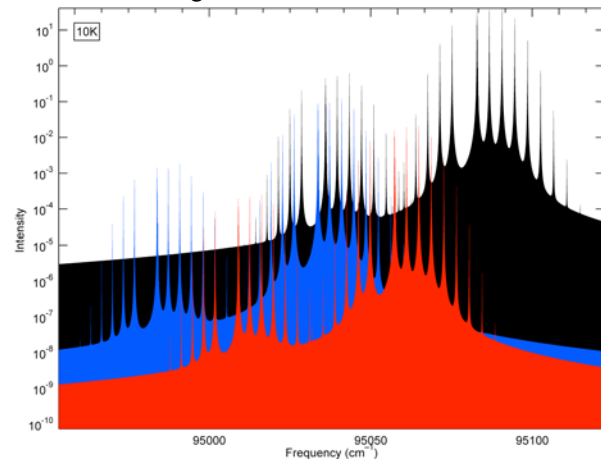temperatures would lead to more mutual shielding and less self-shielding.

Fig. 4. Synthetic absorption spectrum for CO band 37 at 10K. Colors are the same as in Fig. 2.

10K. The temperature is molecular clouds is typically 10–20K. A synthetic spectrum for 10K is shown in Fig. 4. There are even fewer lines than at 50K, and there is little mutual shielded. The fraction of each isotopomer that is not mutually shielded by another isotopomer is: $C^{16}O$–100.0%; $C^{17}O$–84.7% and $C^{18}O$–97.6%. Self-shielding can occur along a slope ~1 line on a three-isotope plot. Non-mass-dependent isotopic fractionation of oxygen is observed in molecular clouds [10].

Conclusions and Caveats: In the synthetic spectra presented here, the lifetimes of all of the lines, which control the natural linewidth, are assumed to be the same. Natural spectra are not quite as neat and well-behaved as those shown here, because of interactions among different isotopomers that lead to longer lifetimes [9]. However, the lifetimes of less than 10% of the lines are so affected. It appears that at high temperature, no self-shielding of $C^{17}O$ occurs via band 37 and that even at 50K fractionation will not occur along a slope ~1 line on the oxygen three isotope plot, although an absorption calculation has not yet been done. It may be that other bands have longer lifetimes and narrower natural linewidths and could be effective at higher temperature.

References: [1] Clayton R. N. et al. (1973) *Science*, *182*, 485–488. [2] Thiemens M. H. and Heidenreich J. E. III (1983) *Science*, *219*, 1073–1075. [3] Clayton R. N. (2002) *Nature*, *415*, 860–861. [4] Shu F. H. et al. (1996) *Science*, *271*, 1545–1552. [5] Lyons J. R. and Young E. D. (2005) *Nature*, *439*, 317–320. [6] Yurimoto H. and Kuramoto K. (2004) *Science*, *305*, 1763–1766. [7] van Dishoeck E. F. and Black J. H. (1988) *Astrophys. J.*, *334*, 771–802. [8] Eidelsberg M. et al. (1991) *Astron. Astrophys. Suppl.*, *90*, 231–282. [9] Ubachs W. et al. (2000) *J. Chem. Phys.*, *113*, 547–560. [10] Sheffer Y. et al. (2002) *Astrophys. J.*, *574*, L171–L174.